

Highly Effective Hydrophilic Modified Carbon Microspheres for Electrochemical Double-layer Capacitors

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In this work, hydrophilic poly(N-vinylpyrrolidone) (PVP) were covalently attached to carbon microspheres (CMS) using the surface-initiate atom transfer radical polymerization method. The synthesis of the materials involves the functionalization of CMS carbon a covalent attachment of PVP. Chemical and morphological changes of the PVP-modified carbon microspheres surface were characterized in detail by X-ray fluorescence spectroscopy and scanning electron microscopy (SEM). Compared with the unmodified CMS, the modified carbon (P-CMS) show higher hydrophilic and have better wettability in an aqueous electrolyte. Owing to the enhanced surface affinity between carbon electrode and electrolyte ions, the P-CMS electrode exhibits much higher capacitance (230 F/g) than the CMS electrode (99 F/g) and better capacitance retention capability. The sample also showed an excellent cycling stability with only about 9% capacity decay at 0.5 A/g after 3000 cycles in 2 M KOH electrolyte. The easy surface modification method of carbon materials and smart capacitive performance of P-CMS makes it a promising electrode material for supercapacitors.

Keywords: Hydrophilic; supercapacitor; carbon microspheres; atom transfer radical polymerization; poly(N-vinylpyrrolidone)

1. INTRODUCTION

In the past few years, carbon electrode materials for electrochemical double-layer capacitor (EDLCs) have been widely investigated, because of its high conductivity, lower resistance, good stability, power density as well as a wide potential window [1, 2]. For carbon-based materials, the capacitance of EDLCs comes from electrostatic forces generated at the interface between the electrode and the electrolyte; thus, performance is strongly dependent on physical and chemical properties of their electrode materials [3]. The pure carbon material is highly hydrophobic surface, the poor

electrolyte-electrode contact and the access for the electrolyte ions to all the active electrochemical surfaces [4], thus limits the effective surface area of the material. So, in order to enhance the capacitance performance, people are paying more attention to improve its wettability toward water for an ideal EDLCs electrode material.

Increasing the capacitance by optimization of the wettability of electrode material has become an increasingly important research field [5]. Thus, chemical modification of electrodes with heteroelements, such as nitrogen, oxygen or phosphorus surface functional groups, have been tested in the past decade [6-10]. Song et al. [11] prepared nitrogen- and oxygen-containing activated carbon nanotubes with high capacitance (327 F/g at the current density of 10 A/g) and good rate capability as supercapacitors electrode. They confirmed that the enhancement of specific capacitance is attributed to the introduced pseudocapacitance by heteroatoms and the improved electrolyte wettability by modifying polarity of carbon matrices. Lee et al. [12] design the surface modified MWCNTs with hydrophilic sulfonate groups (R-SO₃), which shows a good electrolyte affinity with homogeneous dispersibility in water and a superior capacitance. But, the pseudocapacitance usually cannot sustain fast charge/discharge rates neither a high degree of reversibility, which are detrimental to the performance of the electrode materials [13]. Hence, we propose that we can improve the electrochemical performance through ameliorating the wettability of electrode materials by grafting electrolyte-philic polymer on the surface of electrodes, while without sacrificing other outstanding properties.

Another method of covalent hydrophobic functional groups grafted at the surface of carbon materials is currently attracting great attention. Compton et al. reported a facile method of covalently modify the surface of graphite powders with aminophenyl groups [14]. Belanger et al. [15] reported that carbon material grafted by a polyacrylic acid layer with high hydrophilic in an aqueous electrolyte and showed better electrochemical performance than that of unmodified carbon. Furthermore, Zhang et al. [16] have recently reported the grafting of hydrophilic poly(N-vinylpyrrolidone) (PVP) on ordered mesoporous carbon electrode by electrochemically induced surface-initiated atom-transfer radical polymerization, which shows a good surface-hydrophilic and a superior double layer capacitance. Covalent functionalization of the surface of active electrode materials enables to keep the inherent properties of the active materials while demonstrating to be an effective route to improve the performance of supercapacitors. Hence, we propose that we can improve the electrochemical performance through ameliorating the wettability of electrode materials by grafting electrolyte-philic polymer on the surface of electrodes, while without sacrificing other outstanding properties. Hence, it is easy to think about that designing synthesis of electrolyte-philic carbon materials through grafting hydrophilic functional groups on its surface by ATRP, which could be desirable for supercapacitor application.

In this work, we successfully introduced strong hydrophilic PVP onto the surfaces of carbon microspheres (CMS) by ATRP grafting method for supercapacitors. The structural, chemical and electrochemical properties of the materials have been studied in detail. High capacitance (230 F/g), excellent rate performance (79.1%) and long-term stability (91%) of the prepared materials were achieved in 2 M KOH aqueous solution. The way exhibits great potential for fundamental research

about hydrophilic properties of CMS, which exhibits potential applications as an efficient electrode material for supercapacitors.

2. EXPERIMENTAL

2.1. Materials

2-Bromoisobutyryl Bromide (BIBB, Alfa Aesar); triethylamine (TEA), N,N,N,N-tetramethylethylenediamine (TMEDA, Alfa Aesar); Tetrahydrofuran (THF); N,N-dimethylformamide (DMF, AR, Tianjin, China) and methanol (Me(OH), AR, Tianjin, China); $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuBr} \cdot 2\text{H}_2\text{O}$ (AR, Tianjin, China) were purchased and used as received. All other chemicals were of analytical grade and used without purification. Deionized water was used in the experiments.

2.2. Preparation of PVP-modified CMS

2.2.1. Preparation of initiator-functionalized on carbon surface

The progress of initiator-immobilization on the CMS surface can be concluded as follows: i) the hydroxyl groups were introduced on the CMS surface, which synthesized according to the previous publication [17]. The obtained CMS was immersed into nitric acid solution at the temperature of 80°C under refluxing process for 4 h. Then, the samples were washed thoroughly with distilled water. And, CMS with hydroxyl groups were obtained. ii) the initiator of ATRP was immobilized on the surface of CMS by reaction with BIBB. The 0.3 g sample of CMS-OH was dissolved in THF (30 mL) with 1.5 ml of TEA, and the reaction flask was placed in an ice bath. Then, a mixture of 3 mL of BIBB in 20 mL THF was slowly added to the reaction mixture, and then the solution was stirred for 6 h at 0°C and then transferred into 60°C water bath for another 24 h at room temperature. The obtained initiator-functionalized material (CMS-BIBB) was clean thoroughly by methanol, and deionized water, respectively; and then dried overnight under vacuum.

2.2.2. ATRP method of VP on CMS (P-CMS)

A typical ATRP method of VP on the surface of carbon materials takes place in a mixture solution of TMEDA (0.06 g), CuBr_2 (0.09 g), CuBr (0.12 g), degassed VP (4.26 g) monomer and in 45 mL solution of 2:1 (v/v) H_2O /methanol [18]. Before polymerization, the mixture solution were degassed several cycles and backfilled with nitrogen. The mixture solution was kept in a 60°C water bath for a predetermined period of time. Finally, the sample was cooled to stop the polymerization. The sample were washed with methanol/water 1:1 (v/v) contained TMEDA to remove copper traces for several times. And the sample was obtained, which was named as P-CMS.

The preparation of PVP grafted CMS was summarized in Fig.1, which mainly involves the following basic steps. i) Preparation of CMS-OH: the introduction of hydroxyl groups on the surface of carbon-scaffold was carried out by acid treatment; ii) Preparation of initiator-functionalized CMS-BIBB; the initiator of ATRP was immobilized on the surface of carbon-scaffold by the reaction between hydroxyl groups with BIBB; iii) ATRP of VP to graft PVP onto initiator-functionalized CMS surface. Fig. 2a and b shows the surface view of the CMS and P-CMS, respectively. From the surface SEM image in Fig. 2, it can be seen that uneven granular structure on the grafted CMS surface and the CMS surface becomes rougher after the grafting of PVP. These results showed that there are small differences between the unmodified and modified CMS, indicating that PVP polymer chains may grafted onto the CMS surface.

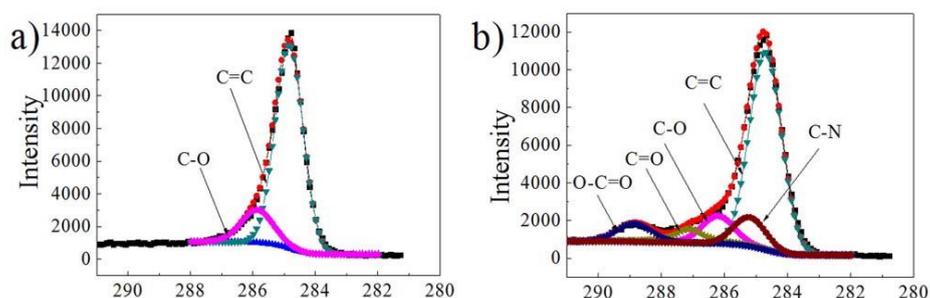


Figure 3. C1s XPS results of the CMS and P-CMS.



Figure 4. Water contact angle of CMS and P-CMS.

XPS was used to characterize the functional groups of unmodified and modified CMS, which provide important information of the material. From XPS test in Fig. 3, nitrogen (N) quantity percentage increased from 1.04% to 5.3% and the (O) quantity percentage increased from 7.8% to 19.0%, which indicated that the PVP chain on the CMS surfaces. In the unmodified CMS, there are two typical peaks corresponding to C=C (binding energy, 284.9 eV) and C-O (binding energy, 286.7 eV) resolved from the C1s core level spectrum [19]. In the case of grafted CMS, the new peaks at 287.7 eV and 289.1 eV are assigned to C=O and O-C=O species of the grafted PVP chain, showing the

change of the surface elemental compositions from CMS. The species fractions of C-N and C=O quantity percentage separately increased from 0.0% and 0.0% to 9.6% and 5.98%, respectively, indicating a significant amount of N- and O-containing groups. And, the results of XPS illustrate that the PVP is successfully grafted onto the CMS-PVP samples. Notably, the increase concentration of heteroelements, such as nitrogen, oxygen surface functional groups concentration, is more important for the modified carbons, presumably because they are more hydrophilic [20]

The water contact angle shows the surface properties (e.g., hydrophilicity and hydrophobicity) of the PVP grafted and unmodified CMS. As is shown in Fig. 4, the contact angle was significantly decreased from 102.5° of CMS to 40° of P-CMS. The reason may be that the polar group of acylamino existing in PVP is more hydrophilic, which can provide fast ion response and increase electrolyte accessibility at the surface of carbon electrode materials [16]. This hydrophilic property of the carbon materials could be useful for its application as electrode in aqueous electrolyte-based supercapacitors. An increase in hydrophilic could potentially enhance the double-layer charge storage behavior, which has been observed for grafted hydrophilic PAA on carbon black in accordance with Belanger et al with a drastically water contact angle decreased to 14° [15, 21].

3.2 Electrochemical performance

Fig. 5a and b shows the CVs of the prepared CMS and P-CMS electrodes in 2 M KOH solution at different scan rates ranging from 5 to 50 mV s⁻¹. All the curves is closely a rectangular shape, indicating that both CMS and P-CMS electrodes mainly contributes to EDLCs [22, 23]. As shown in Fig. 5a and b, the specific capacitance of P-CMS electrodes is higher than CMS electrodes, because of the P-CMS electrodes exhibit larger CV areas than CMS electrodes. Moreover, comparing the shape of the CVs of both samples, P-CMS irreversible processes are less important, revealed smaller polarization. The significantly enhanced capacitance can be attributed to the improvement of wettability after grafting electrolyte-philic PVP, the electroactive surface area is maximized.

Fig. 5c and d display the galvanostatic charge-discharge curves of the prepared carbon materials from 0.5 A/g to 5 A/g, in which all the curves show a good linear symmetry, implying a good electrochemical reversibility and capacitive performance. For CMS and P-CMS electrode materials, the specific capacitance was found to be 99 F/g and 230 F/g at 0.5 A/g. With the current density increased, the specific capacitance decreased. The specific capacitance of the both samples is 68 F/g and 181 F/g, respectively, with a high loading current density of 5 A/g. Fig. 5c and d demonstrates the superior rate ability of the P-CMS electrode, compared to the electrode of CMS.

The above results clearly reveal that P-CMS exhibit significantly improved electrochemical performance compared with CMS. The relatively good capacitive performance of the P-CMS is due to: (1) the presence of the grafted hydrophilic PVP can possess a high concentration of surface functional groups, which can enhance the electroactive surface area for double-layer charge storage; (2) with good contact between the P-CMS and the electrolyte that has contribute to fast transport of ions in the active electrode layer, thus would increase the accessibility of the available pores.

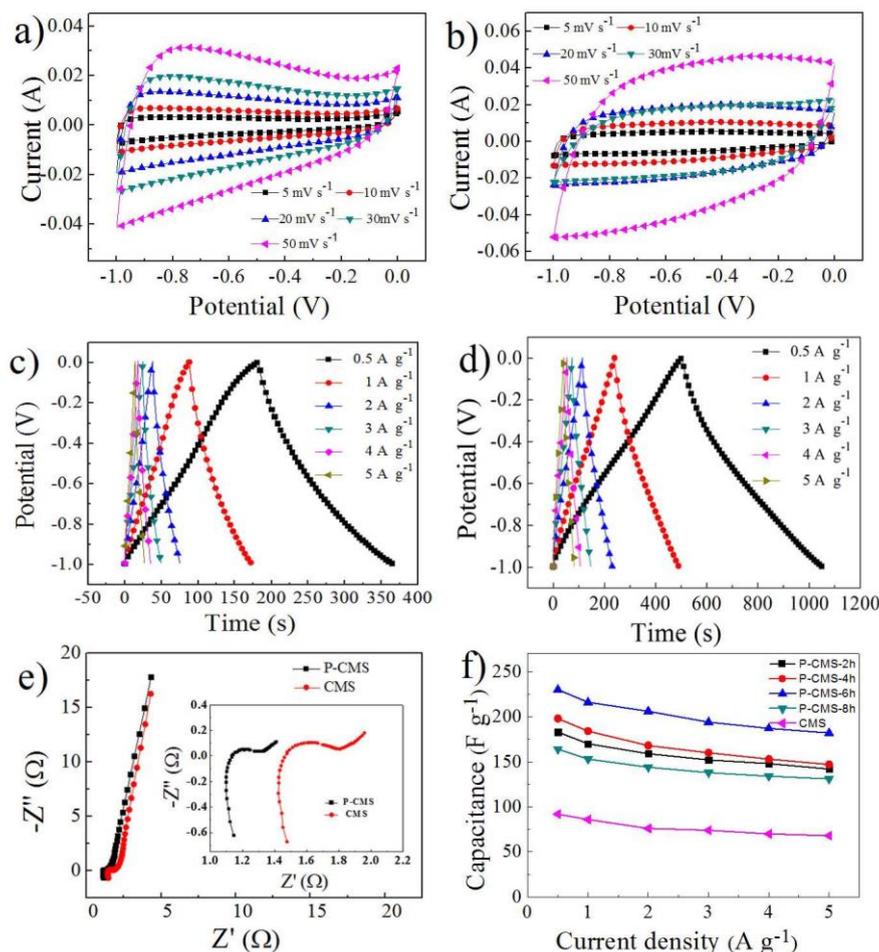


Figure 5. Electrochemical capacitance performance of CMS and P-CMS electrode: (a, b) cyclic voltammetry curves; (c, d) galvanostatic charge-discharge curves; (e) complex-plane impedance plot; (f) relationship between specific capacitance and current density.

To further test these suggested advantages of the P-CMS electrode, the electrochemical impedance spectroscopy (EIS) tests were carried out as shown in Fig. 5e. The intercept of high-frequency semicircle with the real axis in the EIS reflects the internal resistance of electrode (R_b), hence mirroring the of electrode materials [24]. The result shows that the R_b of the P-CMS electrode and the CMS electrode is about 1.1 Ω and 1.5 Ω , respectively, indicating the better conductivity of P-CMS compared with the CMS. While the semicircle diameter of the P-CMS electrode in the high frequency region of EIS is smaller than that of the CMS electrode, suggesting its lower charge transfer resistance. This is probably caused by the good contact between the P-CMS and the electrolyte, which can provide fast transport of ions in the active electrode layer, thus would increase the accessibility of the available pores.

The relationships between specific capacitance value and charge-discharge current density measured in a three-electrode system are presented in Fig. 5f. The specific capacitance of P-CMS firstly increases and then decreases with the increase of the polymerization time. And, a slight decrease in the specific capacitance of P-CMS 6 h is observed as the current densities from 0.5 to 5 A/g, but the

specific capacitance is maintained quite well under higher current densities, for example, the specific capacitance is retained 79.1% (68.7% for the CMS), indicating this electrode material exhibits a good capacitance retention capability. Compared to electrochemical performance of CMS, the overall better property of P-CMS can be mainly attributed to the better wettability in aqueous electrolyte.

For supercapacitors, a long cycle life is among the most important criteria. Thus an endurance test for P-CMS electrode was conducted using galvanostatic charging-discharging cycles at 0.5 A/g (Fig. 6). After 2000 charge/discharge cycles, the maintaining of specific capacitance is 91% at 0.5 A/g. A typical constant current charge-discharge curve for the P-CMS electrode is displayed inset in Fig. 6. The $E-t$ responses of the charge process reveal almost the mirror image of their corresponding discharge counterparts, and no IR drop is observed, demonstrating excellent electrochemical stability of P-CMS electrode. Taken together, our results demonstrate that the P-CMS electrode gives a large specific capacitance and excellent cycling stability, promising for the development of high-performance supercapacitors.

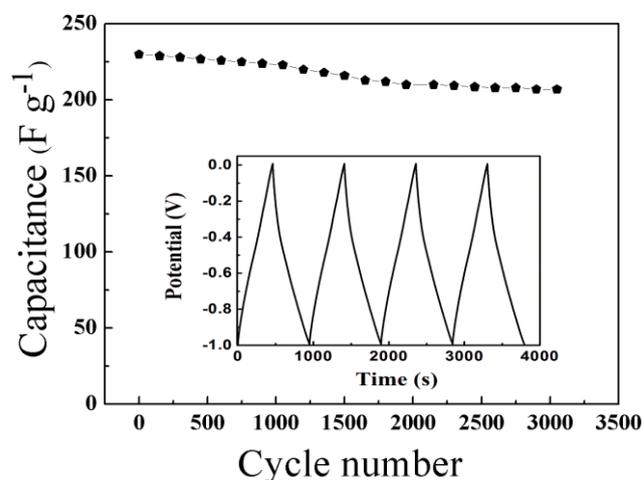


Figure 6. The long-term cycling stability of the P-CMS electrode under a constant current density of 0.5 A/g.

4. CONCLUSION

A novel method to improve the surface hydrophilicity of CMS by ATRP method is reported. Structure and composition analyses reveal that hydrophilic PVP polymer chains were successfully grafted onto the surface of CMS. The presence of the grafted hydrophilic PVP can possess a high concentration of surface functional groups, which can enhance the electroactive surface area for double-layer charge storage. As the electrode material for EDLCs, the P-CMS electrode shows high specific capacitance of 230 F/g, excellent rate performance (79.1%) and long-term stability of the prepared materials were achieved in 2 M KOH aqueous solution. The innovative way exhibits great potential for fundamental research about hydrophilic properties of CMS, which exhibits great potential for using as an efficient electrode material for supercapacitors.

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References

1. B. Fang, Y. Z. Wei and M. Kumagai, *J. Power. Sources*. 155 (2006) 487.
2. A.S. Aricò, P. Bruce, B. Scrosati, J. M. Tarascon, W. Van Schalkwijk, *Nat. Mater.* 4 (2005) 366.
3. Y.F. Deng, Y. Xie, K.X. Zou, X.L. Ji, *J. Mater. Chem. A* 4 (2016) 1144.
4. D.S. Dhawale, G.P. Mane, S. Joseph, C. Anand, K. Ariga, A. Vinu., *Chem. Phys. Chem.* 14 (2013) 1563.
5. B. Fang, Y.Z. Wei, M. Kumagai, *J. Power Sources* 155 (2006) 487.
6. S. Sepehri, B.B. García, Q. Zhang, G. Cao, *Carbon* 47 (2009) 1436.
7. Z. Zapata-Benabithé, F. Carrasco-Marín, C. Moreno-Castilla, *J. Power. Sources* 219 (2012) 80.
8. D. Hulicova-Jurcakova, M. Seredych, Q. L. Gao, T.J. Bandosz, *Adv. Funct. Mater.* 19 (2009) 438-447.
9. M.M. Titirici, A. Thomas, M. Antonietti, *J. Mater. Chem.* 17 (2007) 3412.
10. R. T. Chiang, R. K. Chiang, F. S. Shieu, *RSC Adv* 38 (2015) 6123.
11. H. Liu, H. Song, X. Chen, S. Zhang, J. Zhou, Z. Ma, *J. Power. Sources* 285 (2015) 303.
12. H. Yoo, M. Min, S. Bak, *J. Mater. Chem. A* 2 (2014) 6663.
13. K.W. Leitner, B. Gollas, M. Winter, J.O. Besenhard, *Electrochim. Acta* 50 (2004)199.
14. A.T. Masheter, G.G. Wildgoose, A. Crossley, J.H. Jones, R.G. Compton, *J. Mater. Chem.* 17 (2007) 3008.
15. B.D. Assresahegn, D. Bélanger, *Adv. Funct. Mater.* 25 (2015) 6775.
16. J. Zhang, X.B. Yi, W. Ju, H.L. Fan, Q.C. Wang, B X. Liu, et al. *Electrochem. Commun.* (2016) DOI:10.1016/j.elecom.2016.09.011.
17. X.X. Zhang, F. Ran, H.L. Fan, Y.T. Tan, L. Zhao, X.M. Li, *J. Energ. Chem.* 23 (2014) 82.
18. R.R. Feng, C.C. Wang, X.C. Xu, F.L. Yang, G.J. Xu, T. Jiang, *J. Membrane. Sci.* 369 (2011) 233.
19. H.L. Fan, F. Ran, X.X. Zhang, H.M. Song, W.X. Jing, K.W. Shen, *Electrochim Acta* 138 (2014) 367.
20. A Grondein , D. Bélanger, *Fuel*, 90 (2011) 2684.
21. K.T. Lee, C.B. Tsai, W.H. Ho, N.L. Wu, *Electrochem Commun* 12 (2010) 886.
22. Q.Du, M. Zheng, L. Zhang, Y. Wang, J. Chen, L. Xue, *Electrochim Acta* 55 (2010) 3897.
23. P Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845.
24. B.G. An, S.F. Xu, L.X. Li, J. Tao, F. Huang, X. Geng, *J. Mater. Chem. A* 1 (2013) 7222.